

Diglycol Bis(Carbonates) of Lactic Esters

LACTIC ACID DERIVATIVES AS PLASTICIZERS

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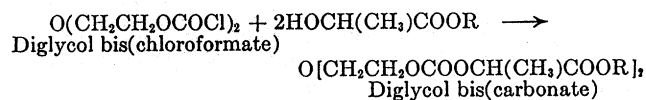
Plasticizers made by acylating twenty-three lactic esters with diethylene glycol bis(chloroformate) $[O(CH_2CH_2OCOCI)_2]$ are described. As a class, these plasticizers were high boiling and compatible with a vinyl chloride-vinyl acetate copolymer, ethylcellulose, and cellulose ace-

tate. The esters prepared from the *n*-butyl, *n*-hexyl, 2-ethylhexyl, 2-butoxyethyl, and 2-(2-butoxyethoxy)ethyl esters of lactic acid were relatively fluid and more efficient than many of the commercial plasticizers in plasticizing the vinyl chloride-vinyl acetate copolymer.

BECAUSE the production of plasticizers in the United States has increased tremendously in the last decade—from 30,000,000 pounds in 1939 to about 190,000,000 pounds in 1949 (1)—much effort has been expended to find improved plasticizers and new raw materials for their manufacture. Lactic acid, commercially available as such and as the methyl, ethyl, and butyl esters,

of interest as a starting material for plasticizers because it can be made easily and efficiently (6, 10) from inexpensive materials such as corn sugar, whey, molasses, and sulfite waste liquor (9); its manufacture is not necessarily associated with or limited by other commercial operations; and having two functional groups, it can be transformed into many high boiling derivatives (6, 14–16) having ester and other compatibilizing groups. Although the preparation of plasticizers from lactic acid has been described (2–6, 15), appreciable quantities have not been used for this purpose.

Considerable work has been done in this laboratory on the preparation and evaluation of high boiling lactic acid derivatives as plasticizers. The present paper describes diglycol bis(carbonates) [diethylene glycol bis(1-carbalkoxyethyl carbonates)] made (15, 16) by acylating certain lactic esters with diglycol bis(chloroformate).



Compatibilities of these bis(carbonates) with cellulose acetate and ethylcellulose and the properties of vinyl chloride copolymer plasticized with the bis(carbonates) are given also. The chemicals required to make most of the bis(carbonates) discussed here are available commercially.

TABLE I. DIETHYLENE GLYCOL BIS(CARBONATES) OF LACTATES

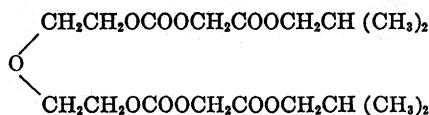
Lactate	Mol. Wt.	B.P., ° C. (15, 16)		Viscosity, Cp.			Water Solubility, G./100 G.	Free Acidity ^b	Boiling Water Stability ^c
		1 mm.	4 mm.	20° C.	40° C.	Ratio ^a			
Methyl	366	195	222	1,818	187.0	0.103	0.22	0.50	492
Ethyl	394	200	228	375.4	70.76	0.188	0.06	0.45	8.5
<i>n</i> -Propyl	422	210	238	309.8	68.61	0.221	0.01	0.10	...
Isopropyl	422	201	230	555.4	88.93	0.160	0.05	0.40	2.2
<i>n</i> -Butyl	450	221	251	206.3	52.80	0.256	0.01	2.05	2.5
Isobutyl	450	215	243	482.2	87.77	0.182	0.01	0.0	0.90
<i>sec</i> -Butyl	450	211	239	476.2	88.22	0.185	0.01	0.50	0.50
<i>n</i> -Hexyl	507	242	271	232.1	59.83	0.258	...	0.50	0.75
2-Ethylbutyl	507	237	265	327.5	75.01	0.229	...	0.25	0.25
4-Methyl-2-pentyl	507	223	252	593.5	96.28	0.163	0.01	1.25	0.05
<i>n</i> -Octyl	563	260	291	204.5	58.6	0.287	...	0.25	0.38
2-Ethylhexyl	563	251	279	307.5	73.18	0.238	...	0.0	0.25
2,6-Dimethyl-4-heptyl	491	242	271	1,313	169.0	0.129	0.01	0.0	2.95
Cyclohexyl	503	251	279	22,565	1092	0.048	0.01	0.60	1.75
Methylcyclohexyl	531	257	285	16,240	832.0	0.051	0.01	1.85	0.65
Allyl	418	215	243	262.9	63.01	0.238	0.03	1.05	...
1-Carballyloxyethyl ^d	563	1,631	115.3	0.076	0.05	0.90	304
2-Methoxyethyl	454	238	266	741.8	127.3	0.172	0.29	0.27	296
2-Ethoxyethyl	482	245	273	431.8	88.33	0.205	0.48	0.10	61.1
2-Butoxyethyl	539	256	285	329.7	77.96	0.237	0.01	0.70	1.45
2-(2-Chloroethoxy)ethyl ^d	551	822.2	155.0	0.189	0.03
2-(2-Butoxyethoxy)ethyl ^d	627	135.5	43.11	0.318	0.08	0.55	33.5
Tetrahydrofurfuryl	506	266	295	4,438	516.0	0.116	0.29	0.35	122.1
Isobutyl glycolate	422	221	249	471.7	93.61	0.199	0.01	0.60	9.90
Diglycol bis(butyl carbonate)	306	165 ^e	175 (3)	20.1	9.7	0.486	0.01
2-Ethylhexyl phthalate/	391	...	229 (5)	84	26	0.310	0.01
Triglycol dihexoate ^f	346	...	202 (5)	17	10.5	0.618	0.02

^a Viscosity ratio = cp. 40°/cp. 20°.^b Ml. *N* NaOH per 100 grams of plasticizer.^c Ml. *N* NaOH per 100 grams of plasticizer after boiling in water for 24 hours.^d Undistilled material.^e Pressure, mm.^f Flexol DOP.^g Flexol 3GH.

EXPERIMENTAL

Redistilled samples of the commercially available methyl, ethyl, and *n*-butyl esters of lactic acid and several other lactic esters prepared as previously described (4, 13, 14) were used. Allyl lactyl lactate (16) [HOCH(CH₂)COOCH(CH₂)COOCH₂CH:CH₂], needed for the preparation of the diglycol bis(carbonate) of 1-carballyloxyethyl lactate, was obtained as a by-product in the preparation of allyl lactate (15). Commercial diglycol bis(chloroformate) was used as received. The lactic esters were acylated with the bis(chloroformate) in the presence of pyridine and ether at about 0° F. The products were washed successively with dilute acid and with water; most of the carbonates were then distilled at reduced pressure. The washed products, however, were almost colorless or light amber, and hence were suitable as plasticizers without distillation. The bis(carbonates) were thermally stable below about 225° to 250° F. The yields, higher than 90% of the theoretical in some instances, were usually good. Analytical data, including carbon and hydrogen contents, saponification equivalents, and molecular refractions were in agreement with the theoretical value (15, 16).

The diglycol bis(carbonate) of isobutyl glycolate was prepared, and its properties were compared directly with those of the



diglycol bis(carbonate) of isobutyl lactate (Table I).

Compatibilities (Table II) with cellulose acetate and ethyl-cellulose were determined by examining plasticized films of these materials prepared by casting from solutions. Clear, transparent films indicated compatible plasticizers.

Because large quantities of plasticizers are used with vinyl chloride polymers, most attention was given to compositions containing the bis(carbonates) and Vinylite VYDR, a 95% vinyl chloride-5% vinyl acetate copolymer. The formulation, as follows, and milling procedure have been described (17, 18):

	Parts
Vinyl chloride copolymer	63.5
Basic lead carbonate	1.0
Stearic acid	0.5
Plasticizer	35.0

Tensile properties of molded compositions were obtained from A.S.T.M. Type D dumbbell test specimens cut from a 0.065-inch thick slab molded at 300° F. in a sandwich-type mold with polished ferrotype face plates. The tensile test was performed on a Scott IP-4 inclined plane machine in accordance with A.S.T.M. D 882-46T except for the width of the test specimen. The rate of loading was 80 pounds per minute. Modulus was obtained at 100% elongation by tapping the autographic chart lightly to form a "pip" on the curve at the instant the specimen had elongated 100% between bench marks.

Brittle points of the copolymer compositions were determined with small samples cut from molded sheets or slabs (approximately 0.065 inch thick); equipment similar to that of Selker, Winspear, and Kemp (19) was used.

An estimate of the stability to heat was obtained by heating small squares of the molded sheets (0.08 inch thick) in an oven at 150° C. and observing them at hourly intervals. Of those tested, the alkyl derivatives were most stable; they showed no appreciable discoloration after 7 hours. The alkoxyethyl esters showed little change, but the tetrahydrofurfuryl ester (undistilled material) darkened in 4 hours. Free acidity and stability to boiling water of the esters were determined by the method of Fordyce and Meyer (7).

PROPERTIES OF BIS(CARBONATES)

The bis(carbonates) were dense liquids (*d*₄²⁰ always higher than 1) having molecular weights ranging from 366 to 627. In spite of their relatively high content of oxygen, they were insoluble in water (Table I). They differed greatly in their stability toward boiling water, the esters of high oxygen content being relatively unstable (Table I).

As a class, the bis(carbonates) were more viscous (Table I) than several of the plasticizers reported to be efficient in softening vinyl chloride polymers (11, 12, 17, 18). The less viscous bis(carbonates) were characterized by relatively long straight chains—that is, such as those made from *n*-butyl, *n*-hexyl, *n*-octyl, and 2-(2-butoxyethoxy)ethyl lactates. As is evident from the viscosities of the cyclohexyl, methylcyclohexyl, and tetrahydrofurfuryl esters, rings were particularly effective in increasing viscosity. Branching usually increased the viscosity appreciably. Comparison of the viscosities of the isobutyl glycolate and isobutyl lactate esters indicates, however, that the side methy-

group of the lactic acid segment is relatively ineffective in raising the viscosity.

The temperature coefficient of the viscosities (Table I) was usually greater than that of the commercial plasticizer, 2-hylhexyl phthalate. It has been suggested (1, 12) that relatively fluid plasticizers having viscosities little influenced by temperature are usually efficient. The results of the present work are in general agreement with this statement.

Even the more volatile bis(carbonates) had high boiling points, comparable with that of octyl phthalate (8) and higher than those of many commercial plasticizers (Table I). Because of their high boiling points, the bis(carbonates) should be outstanding in permanence.

PLASTICIZED COMPOSITIONS

Table II gives the compatibilities of the bis(carbonates) with a 95% vinyl chloride-5% vinyl acetate copolymer (Vinylite VYDR), cellulose acetate, and ethylcellulose. Those data show that the bis(carbonates) as a class are compatible with these resins, presumably because of the abundance of ester groups. The bis(carbonates) of the lower alkyl lactates were incompatible with the vinyl chloride resin but compatible with cellulose acetate. As the size of the alkyl group increased, compatibility with the vinyl chloride resin improved, and compatibility with cellulose acetate decreased. All the bis(carbonates) higher than the hexyl ester (Table II) were incompatible with cellulose acetate. A similar trend in the alkoxyethyl series (Table II) is suggested, but the data are not adequate for broad generalizations. In general, the esters containing the least oxygen were most compatible with the vinyl resin and least compatible with cellulose acetate. Many of the bis(carbonates), however, were compatible with both the vinyl chloride resin and cellulose acetate. All the bis(carbonates) were compatible with ethylcellulose (Table II).

Branched chain and secondary alkyl esters (Table II) appeared to be slightly more compatible than the *n*-alkyl esters but less efficient in plasticizing the vinyl chloride resin.

As judged by modulus values (Table II), several of the plasticizers approached 2-ethylhexyl phthalate, the most widely used plasticizer for vinyl chloride resins, in efficiency. In general, the relatively fluid esters were more efficient and produced compositions having lower brittle points than the viscous esters.

A comparison of the compositions plasticized with the bis(carbonates) of butanol on one hand and *n*-butyl lactate on the other suggests that bis(carbonates) of *n*-alkanols are more efficient plasticizers than the corresponding derivatives of *n*-alkyl lactates. This improved efficiency of the simpler *n*-alkanol ester might be due in part to lower molecular weight.

The data obtained with the bis(carbonate) of isobutyl glycolate (Table II) indicate that this ester is more efficient than the corresponding derivative of isobutyl lactate. The lactate, however, is considerably more resistant to water (Table I).

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TABLE II. PLASTICIZING ACTION OF DIETHYLENE GLYCOL BIS(CARBONATES) OF LACTATES

Lactate	Polyvinyl Chloride-Acetate ^a				Compati- bility ^b , Cellulose Acetate ^c
	Tensile strength, lb./sq. inch	Elonga- tion, %	Modulus at 100% elonga- tion, lb./sq. inch	Brittle point, ° C.	
Methyl ^d	I	240	2310	-13	C
Ethyl	I	240	1920	-10	C
Propyl	3560	290	2210	-8	C
Isopropyl	3540	270	1870	-7	C
Butyl ^d	3480	300	2020	-8	C
Isobutyl	3640	330	2080	-8	C
sec-Butyl	3960	290 ^d	1890 ^d	-8 ^d	C
Hexyl	3140	300	1510	-16	CI
2-Ethylbutyl	3260	320	1570	-14	C
2-Methyl-2-pentyl- octyl	3580	300	2560	-1	C
	3690 ^d	270 ^d	2330 ^d	-20 ^d	C
	3440	320	1590	-17	I
2-Ethylhexyl	3330	330	1570	-14	I
2,6-Dimethyl-4- heptyl	3360	310	1890	-9	I
Cyclohexyl ^d	3440	<100	...	19	CI
Methylcyclohexyl ^d	3820	<100	...	21	CI
Allyl	CI 2790	180	2590	16	C
1-Carballyloxy- ethyl ^c	I	C
2-Methoxyethyl ^d	I	C
2-Ethoxyethyl ^d	I	270	2320	...	C
2-Butoxyethyl ^d	3800	250	2510	-17	C
2-(2-Butoxyethoxy) ethyl ^d	3200	290	1810	-21	C
2-(2-Chloroethoxy) I ethyl ^d	C
Tetrahydrofurfuryl ^d	3750	270	2780	0	C
Isobutyl glycolate	3490	300	1740	-16	C
2-Ethylhexyl phthalate	3070	290	1500	-32	...
Triglycol dihexoate	2690	290	1170	-59	...
Diglycol bis(butyl carbonate)	3130	310	1090	-39	...

^a Vinylite VYDR, Carbide and Carbon Chemicals Corp., (35% plasticizer).

^b All bis(carbonates) were compatible with ethylcellulose in the ratio of 1 to 3; C = compatible; I = incompatible.

^c Hercules Powder Co.'s FM-6 (25% plasticizer; films cast from solution).

^d Undistilled material used.

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